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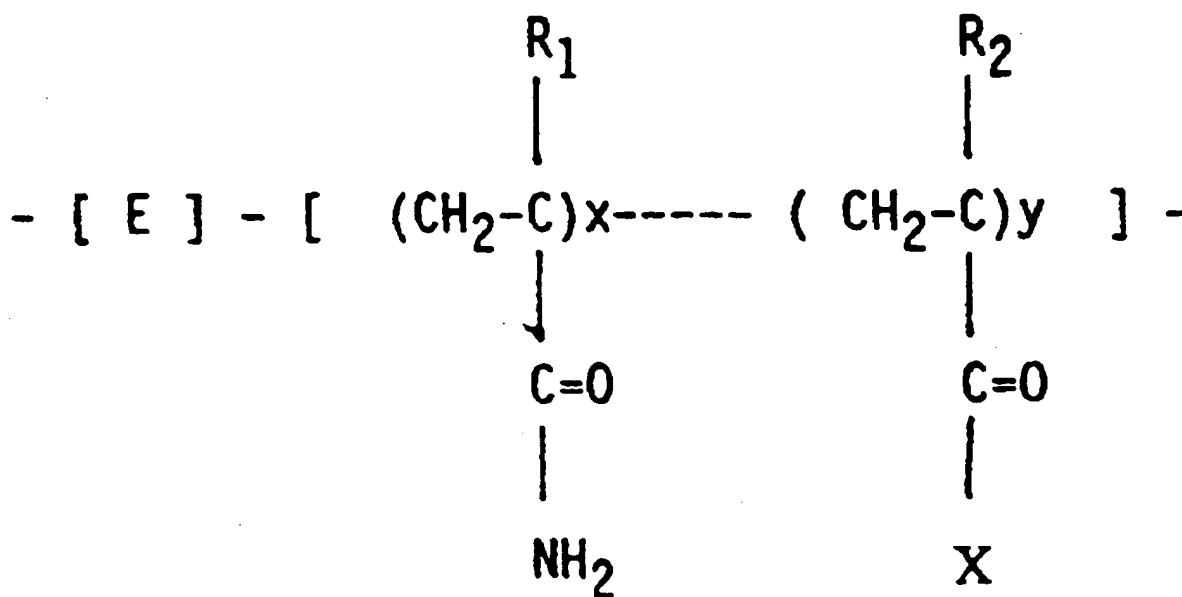LIAO, WEN P., US;
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(54) Titre : COPOLYMERES SEQUENCES SOLUBLES DANS L'EAU ET MODES D'UTILISATION
(54) Title: WATER SOLUBLE BLOCK COPOLYMERS AND METHODS OF USE THEREOF

(57) Abrégé/Abstract
A composition and method of use thereof for the treatment of wastewater comprising a block copolymer having the formula:
(see above formula) wherein E is a polymeric segment obtained from the polymerization of hydrophobic monomers, x when present is a nonionic monomer, y is a cationic monomer, R_1 and R_2 are the same or different and are H or a lower alkyl group from C_1 to C_3 and X is a salt of an ammonium cation.

WATER SOLUBLE BLOCK COPOLYMERS
AND METHODS OF USE THEREOF

FIELD OF THE INVENTION

5   The present invention relates to water soluble block
copolymers containing water soluble and water insoluble monomers
which are useful for water treatment, especially sludge dewatering
and water clarification.

BACKGROUND OF THE INVENTION

There is an increasing usage of water soluble polymers and
10   copolymers in wastewater treatment industries. These compounds
have shown desirable utility for the purpose of dewatering sludge
and clarifying contaminated water.

The efficacies of the polymers or copolymers used will vary
depending upon the type of monomers chosen to form the polymer or
15   copolymer, the molecular weight of the synthesized molecule and, in
the case of a copolymer, the placement of the selected monomers on
the backbone of the copolymer. It is the latter characteristic
that is the focus of the present invention.

Copolymers may be synthesized without attention to the distribution of the two base monomers along its backbone resulting in a random distribution of these monomers. Synthesis may be controlled, however, to form a copolymer having long sequences of monomers, eg. A and B, as follows:

5

- AAAA - BBBB - AAAAA - BBBBB -

This formation results in compounds referred to as block copolymers.

Block copolymers exhibit unique properties and as a result are more desirable than random copolymers or a blend of the two homopolymers synthesized from the respective monomers. The industrial importance of block copolymers has increased markedly in recent years for these reasons.

10

RELATED ART

15

U.S. Patent 4,492,785 describes water soluble block polymers of t-butylstyrene/styrene sulfonate and t-butylstyrene/ styrene sulfonate/t-butylstyrene. The preparation process requires sequential anionic polymerization, sulfonation, separation and purification. The product is used as a viscosification agent.

20

U.S. Patents 4,521,580 and 4,528,348 disclose a method of using surfactants to solubilize water insoluble monomers such as octyl acrylamide in order to copolymerize with acrylamide.

U.S. Patent 4,906,716 discloses a process of incorporating hydrophobic water insoluble monomers, such as alkyl acrylamides which are solid at room temperature, with acrylamide into a water soluble copolymer. The process involves heating the hydrophobic

5   water insoluble monomers to above their melting point.

U.S. Patent 4,835,234 discloses hydrophobically associating terpolymers containing acrylamide, cationic monomer and water insoluble monomers such as higher alkylacrylate or alkylamide. All monomers are mixed together in solution prior to a micellar poly

10   merization. The resulting polymers are random copolymers in nature.

U.S. Patent 3,984,333 teaches using a water-soluble block copolymer having water-soluble blocks and water-insoluble blocks for an oil recovery process. While such water-soluble block co

15   polymers exhibit reasonably good resistance to shear degradation, such polymers are difficult and often impractical to prepare. While polymers containing hydrophobic or water insoluble groups are disclosed, none have the same configuration as disclosed in this invention. The hydrophobic or water insoluble groups in the

20   polymer of this invention are not randomly distributed as in the related art, but form a polymeric segment attached to a polymer chain obtained from copolymerization of acrylamide and cationic monomers. The resulting polymer has a block copolymer structure and shows unique solution properties. As the polymer is placed

25   in an aqueous solution, the hydrophobic segments aggregate or

associate in a manner similar to a surfactant. The association between polymer chains results in an increase in the hydrodynamic size, which in turn, causes an increase in solution viscosity.
As a result, the block copolymers in this invention are quite

5 effective in sludge dewatering applications as compared to the commercial or related art materials with much higher intrinsic viscosities. The new class of water soluble block copolymers can be used at a lower dosage and also shows a wider optimum dosage range than conventional materials. This will lower the treatment

10 cost and reduces the risk of overdose for sludge dewatering, a highly undesirable consequence.
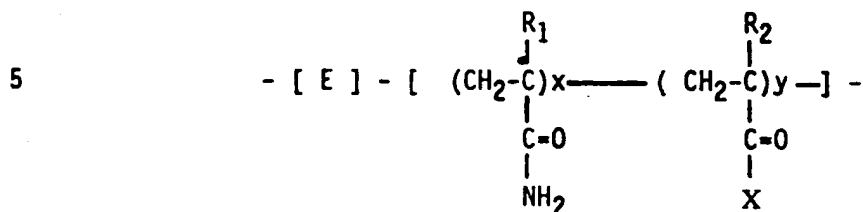

DETAILED DESCRIPTION OF THE INVENTION

The block copolymers of the invention useful for water treatment contain a polymeric segment obtained from polymerization

15 of hydrophobic or water insoluble monomers attached to a polymer chain obtained from polymerization of one or more water soluble monomers. The resulting block copolymers are water soluble.

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The block copolymer of the invention has the general structure:

FORMULA I

$$- [E] - [\ (CH_2-\underset{\underset{NH_2}{\overset{\displaystyle C=O}{|}}}{\overset{\displaystyle R_1}{\underset{|}{C}}})x \text{------} (\ CH_2-\underset{\underset{X}{\overset{\displaystyle C=O}{|}}}{\overset{\displaystyle R_2}{\underset{|}{C}}})y -] -$$

wherein E is a polymeric segment obtained from the polymerization of hydrophobic or water insoluble monomers. Examples of such monomers include alkyl acrylamides, alkyl methacrylamides, alkyl acrylates, alkyl methacrylates, and alkylstyrenes. Preferably, the hydrophobic monomer is an alkyl acrylate having 4 to about 16 carbon atoms in the alkyl group such as 2-ethylhexyl acrylate. Other suitable hydrophobic or water insoluble monomers include the higher alkyl esters of ethylenically unsaturated carboxylic acids such as alkyl dodecyl acrylate, dodecyl methacrylate, tridecyl acrylate, tridecyl methacrylate, octadecyl acrylate, octadecyl methacrylate, ethyl half ester of maleic anhydride, diethyl maleate, and other alkyl esters derived from the reactions of alkanols having from 8 to 20 carbon atoms with ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic anhydride, fumaric acid, itaconic acid and aconitic acid, alkylaryl esters of ethylenically unsaturated carboxylic acids such as nonyl-α-phenyl acrylate, nonyl-α-phenyl methacrylate, dodecyl-α-phenyl acrylate and dodecyl-α-phenyl
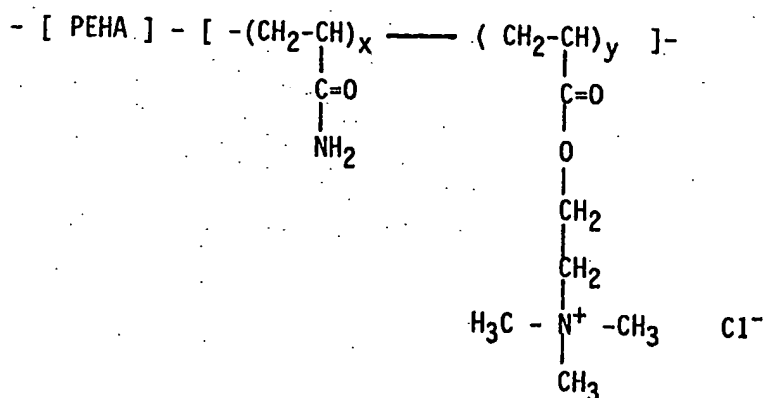
methacrylate; N-alkyl, ethylenically unsaturated amides such as
N-octadecyl acrylamide, N-octadecyl methacrylamide, N,N-dioctyl
acrylamide and similar derivatives thereof; vinyl alkylates
wherein alkyl has at least 8 carbons such as vinyl laurate and
5   vinyl stearate, vinyl alkyl ethers such as dodecyl vinyl ether
and hexadecyl vinyl ether; N-vinyl amides such as N-vinyl
lauramide and N-vinyl stearamide; and aralkylstyrenes such as
t-butyl styrene. Of the foregoing hydrophobic monomers, the
alkyl esters of acrylic acid and methacrylic acid wherein alkyl
10   has from 4 to 16 carbon atoms, are preferred. The hydrophobic
polymers are not water soluble and can be prepared by
precipitation or emulsion polymerization techniques.

Monomer x, when present, in the Formula I is a nonionic
monomer such as acrylamide or alkylacrylamide. R_1 and R_2 is
15   H or a lower alkyl group having C_1 to C_3. Monomer y is a
cationic monomer. X in the above formula is a salt of an
ammonium cation, such as NHR_3N^+ $(R_{4,5,6})Y^-$ or OR_3N^+
$(R_{4,5,6})Y^-$, wherein R_3 is a C_1 to C_4 linear or branched
alkylene group, and R_4, R_5 and R_6 can be selected from the
20   group consisting of hydrogen, C_1 to C_4 linear or branched alkyl,
C_5 to C_8 cycloalkyl, aromatic or alkylaromatic group; and Y^-
is an anion, such as chloride, bromide, or methyl or hydrogen
sulfate. Typical cationic monomers are 2-acryloxyethyltrimethyl
ammonium chloride (AETAC), 3-methacrylamidopropyltrimethyl ammonium
25   chloride (MAPTAC), 2-methacryloylethyltrimethyl ammonium chloride
(METAC) and diallyl dimethyl ammonium chloride (DADMAC), etc.

The molar percentage x:y of nonionic monomer : cationic monomer, may fall within the range of between 0:100 to 95:5. The molar percentages of x and y must add up to 100%. It is to be understood that more than one kind of cationic monomer may be
5   present in the Formula I.

At present, the preferred water soluble block copolymer for sludge dewatering applications is:

FORMULA II

$$- [\text{ PEHA }] - [-(CH_2\text{-}CH)_x \text{----} (CH_2\text{-}CH)_y]-$$

10
                                C=O   C=O

                                NH$_2$ O

                                                 CH$_2$

                                                 CH$_2$

                                         H$_3$C - N$^+$ -CH$_3$ Cl$^-$

15   CH$_3$

wherein PEHA is poly(2-ethylhexyl acrylate) obtained from polymerization of 2-ethylhexyl acrylate (EHA) initiated by a diperoxide initiator, 2,5-dihydroperoxy-2,5-dimethylhexane (Luperox 2,5-2,5, Pennwalt). The resulting poly(EHA) is water insoluble and has a
20   hydrophobic nature. The number average molecular weight (Mn) of poly(EHA) may fall within the range of 500 to 1,000,000.

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Preferably, the number average molecular weight will be within the range of 1,000 to 500,000, with the range of about 5,000 to about 200,000 being even more desirable. The key criterion is that the resulting block copolymer be water soluble. Since the diperoxide
5   initiator is used to initiate EHA, the resulting poly(EHA) still contains peroxide for further reaction. It is then copolymerized with monomers x and y to form a block copolymer.

In this invention, the preferred monomer x is acrylamide and monomer y is 2-acryloxyethyltrimethyl ammonium chloride (AETAC).
10   The molar percentage of x:y is from about 0:100 to 95:5, with the molar percentage of from about 10:90 to 75:25 being preferred. The block copolymers are prepared by a water-in-oil emulsion technique. Such processes have been disclosed in U.S. Patents 3,284,393, Reissue 28,474 and Reissue 28,576.
15   The resulting copolymers may also be further isolated by precipitating it in an organic solvent such as acetone and dried to a powder form. The powder can be easily dissolved in an aqueous medium for use in desired applications.

Branching agents such as polyethyleneglycol di(meth)
20   acrylate, methylene bis(meth)acrylamide, N-vinyl acrylamide, allyl glycidyl ether, glycidyl acrylate and the like may also be added, providing the resulting block copolymer is water soluble. It is to be understood that the aforementioned polymerization methods do not in any way limit the synthesis of polymers according to this
25   invention. Any of the well known chain transfer agents familiar

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to those who skilled in the art may be used to control the molecular weight. Those include, but are not limited to, lower alkyl alcohols such as isopropanol, amines, mercaptans, phosphites, thioacids, allyl alcohol and the like.

5   The structure of the block copolymer is substantiated by a conventional solution viscosity study and C^{13} NMR spectroscopy. The molecular weight of the resulting block copolymer is not critical, as long as it is soluble in water.

EXPERIMENTAL SYNTHESIS OF BLOCK COPOLYMERS

10   Example 1

Peroxide-Containing Poly(2-ethylhexyl acrylate)

          A suitable reaction flask was equipped with a condenser, a thermometer, a nitrogen inlet, and an overhead mechanical agitator. The flask was charged with 150 g of 2-ethylhexyl acrylate
15   (EHA, Aldrich), 8 g of 70% 2,5-dihydroperoxy-2,5-dimethylhexane (Luperox* 2,5-2,5, Lucidol) and 300 g of methanol. The resulting hazy solution was gradually heated to 50°C under nitrogen. A sodium metabisulfite solution (SMB, 1 g in 10 g water) was prepared separately and sparged with nitrogen.

     *trade-mark

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The bisulfite solution was then added slowly to the reaction flask. Almost immediately the slightly hazy solution turned into a white colloidal dispersion and the polymer precipitate gradually formed. After the addition of bisulfite solution was complete, the

5 reaction temperature was raised to 60°C for about 40 minutes. The solvent was then distilled off under reduced pressure at an elevated temperature to give brownish polymer paste. No residual monomer was detected by C^{13} NMR. The resulting polymer was then redissolved in a low volatile oil (Soltrol* 145, Philips Petroleum).

10 The Brookfield viscosity was 780 cps (49.7 % polymer) and the molecular weights determined by gel permeation chromatography was Mn = 9.5 x 10^3, Mw = 7.4 X 10^4 g/mole.

Examples 2-5

Block Copolymers

15 Block copolymers of acrylamide (AM), 2-acryloyloxyethyltri-methyl ammonium chloride (AETAC) and peroxide-containing poly(EHA) of Example 1 were prepared using a water-in-oil emulsion polymerization technique. The typical polymerization procedure is shown as follows.

20 A reaction flask similar to that described in Example 1 was charged with an oil phase which contained sorbitan monooleate, oil and peroxide containing poly(EHA) of Example 1. The exact charges are shown in Table I.

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An aqueous phase was prepared separately which contained acrylamide (AM), 2-acryloyloxyethyltrimethyl ammonium chloride (AETAC), water, and a chelating agent (Table I). The solution was further adjusted with acid to pH 4.5.

5   The aqueous phase was added to the oil phase and the resulting emulsion was further homogenized with a homogenizer to obtain a stable water-in-oil emulsion. The emulsion was purged with nitrogen for 30 minutes.

      The polymerization was initiated by slowly adding a dilute
10   sodium metabisulfite solution (SMB) to the emulsion under nitrogen and the temperature was maintained at 50-85°C by an external cooling. After the addition, the emulsion was held at 50-85°C for 30 minutes. A trace amount of t-butylhydroperoxide (t-BHP) was then added to the emulsion. The emulsion was held at 50°C for an
15   additional 30 minutes before cooled. A blend of surfactants was finally added to the emulsion.

      C^{13} NMR showed that there was no detectable amount of residual monomer in the resulting emulsion. The emulsion readily inverted into an aqueous solution when added to water.

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TABLE I
Preparation of Block Copolymers

Reagents Charged (grams)	Example 2	Example 3	Example 4	Example 5
Sorbitan monooleate	10.47	10.47	12.82	10.16
Example 1, Poly(EHA)	37.78	37.78	37.83	20.00
Soltrol 145	115.93	115.78	145.91	120.63
50% AM	141.02	114.80	89.20	-
79.2% AETAC	89.31	134.45	178.65	175.60
D.I. Water	52.34	56.31	104.31	102.65
Versenex* 80	0.64	0.62	0.53	0.54
SMB	5.00	5.00	5.00	2.65
D.I. Water	10.50	10.03	10.00	10.90
t-BHP (70%)	1.72	1.70	1.70	0.90
D.I. Water	10.33	10.26	10.00	10.09
Tergitol* 15-S-9	16.70	17.50	21.07	15.99
Areosol* GPG	4.18	4.38	5.27	4.00

Soltrol 145 = hydrocarbon oil, Phillips Petroleum
AM = acrylamide
AETAC = 2-acryloyloxyethyltrimethyl ammonium chloride
Versenex 80 = pentasodium diethylenetriamine
                pentraacetic acid solution, Dow
SMB = sodium metabisulfite
Tergitol 15-S-9 = C11-C15 secondary alcohol ethoxylate,
                Union Carbide

Aerosol GPG = dioctyl ester of sodium sulfosuccinic acid,
                American Cyanamid

*trade-mark

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Example 6

Peroxide-Containing Poly(EHA)

    A similar polymerization process as in Example 1 was
utilized. The formulation was as follows:

5

2-ethylhexyl acrylate	60.0 g
Luperox 2,5-2,5	0.7
Methanol	300.0
Sodium metabisulfite	0.6
D.I. Water	5.0

10 After polymerization was complete, a large excess of water was added
to the mixture. The resulting water insoluble poly(EHA) was removed
from the mixture and dried in a vacuum oven. The poly(EHA) obtained
was redissolved in a low volatile oil (LOPS, Exxon) at a polymer
concentration of 16.8% (w/w) and was to be used for Example 7.

15 Example 7

Block Copolymer

    Utilizing the similar procedure described in Examples 2-5,
except that sulfur dioxide (SO_2) instead of SMB was used to acti-
vate the peroxide groups in the poly(EHA) of Example 6. In addition,
20 Luperox 2,5-2,5 (Lucidol*) instead of t-BHP was used to couple with
SO_2 to react with residual monomer. SO_2 was added at once, the
exotherm of the polymerization quickly raised the reaction
temperature to 85°C.

    *trade-mark

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Air was used occasionally to help control the reaction. The resulting polymer was precipitated in acetone and filtered. It was further dried in a vaccum oven to obtain a dry powder. The formulation was as follows:

5	Sorbitan monooleate	8.95 g
		10.35
	Example 6, Poly(EHA)	127.34
	50% AM	137.02
	79.2% AETAC	155.56
10	D.I. Water	89.27
	Versenex 80	0.67
	Luperox 2,5-2,5	0.047
	D.I. Water	5.08

* Atlas G-1086 = polyoxyethylene sorbitol hexa-oleate, ICI

15   The intrinsic viscosities of the resulting block copolymers are shown in Table II.

TABLE II
Block Copolymers

Polymer	Intrinsic Viscosity (dl/g)	% Solids
Example 2	4.3	40.6
Example 3	5.4	42.9
Example 4	3.9	39.6
Example 5	3.8	37.4
Example 7	4.5	----

*trade-mark

PERFORMANCE TESTS

          In the following tests, the performance of the resulting
     water soluble block copolymers described in this invention is
     demonstrated. The Capillary Suction Time (CST) device was used
5   to measure the dewatering performance of the various polymers on
     several different substrates. The CST device consists of an elec-
     tronic timer, a plexiglass cell holder containing two concentric
     electrodes, and a tall stainless steel cylindrical cell. The
     device operates by measuring the drainage of water from a sludge
10   substrate out of the cell. This is accomplished by placing the
     cell holder containing the two electrodes on a piece of Whatman #17
     chromatography paper, 7.0 x 9.0 cm in size. The tall cylinder is
     then placed in the hole in the cell holder. The cell holder is
     connected to the electronic timer, which is turned on and reset.
15   A 7 ml aliquot of the substrate is introduced into the cell. As
     the water migrates out of the cell, it is absorbed onto the chroma-
     tography paper. This results in a migration of a water front
     through the paper. As the water advances, it contacts the first
     electrode, activating the timer. Continued advancement of the
20   water eventually reaches the second electrode, completing the
     circuit and shutting off the timer. The process is repeated for
     several polymer dosages. A dosage response curve plotting CST time
     (in seconds) versus polymer dosage gives an indication of a par-
     ticular polymer's effectiveness in dewatering a substrate. The
25   dosage curve minimum is an indication of the optimum polymer
     dosage, while the extent of the trough gives a measure of the
     polymer's tendency to overdose. Overdosing is observed when the
     CST values increase with increasing polymer dosage.

The following experimental protocol was followed for the
tests conducted:

1. A sample of known volume of sludge (usually 250 ml)
    was placed in a beaker.

5   2. A known amount of polymer from a 0.5% stock solution
        was added to the beaker to give a pre-determined con-
        centration. The 0.5% polymer stock solution was pre-
        pared by adding a known amount of the active polymer
        to a fixed volume of water, and then mixing for 15
10   minutes at 600 rpm using a standard 3 blade mixer.

    3. The treated substrate was mixed for 30 seconds at
        constant RPM using a standard 3 blade mixer.

    4. A 7 ml aliquot was withdrawn from the beaker and
        placed in the CST cylindrical cell.

15 5. The time required for the water to complete the
        eletrode circuit of the CST device was recorded.

    6. The process was repeated until a reasonable dosage
        response was generated.

Test 1:

A sample of mixed primary and secondary sludge from a paper mill
was used as a substrate. For this test, block copolymers of
varying cationic monomer content was evaluated (Table II). Their
5 performance was compared to commercial polymers commonly used for
dewatering at similar percent solids and cationic monomer content.
The commercial polymers tested are given in Table III.

TABLE III
Commercial Polymers Tested

10	Polymer	Intrinsic Viscosity (dl/g)	% Solids
	Polymer A	8.4	42.0
	Polymer B	9.7	42.0
	Polymer C	8.9	43.0
	Polymer D	9.7	45.0

15   Polymers A, B, C and D are acrylamide/AETAC copolymers
commercially available from American Cyanamid and vary
in molar percentages and molecular weights.

The dewatering performance of the various polymers
is shown in Table IV.

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TABLE IV
Dewatering Performance

Polymer	CST(sec) at varying polymer dosages(ppm)			
	100	200	300	400
Example 3	110	80	20	10
Polymer A	190	120	50	20
Example 2	120	100	40	20
Polymer B	100	70	20	10
Example 5	120	30	10	10
Polymer C	260	250	140	200
Example 4	90	20	10	10
Polymer D	160	110	30	10

Blank: 350 sec.

Test 2

In this test, secondary sludge from a petroleum facility was used as the test substrate. The polymers evaluated are shown in Tables II and III. Results of the dewatering evaluation are given in Table V.

TABLE V
Dewatering Performance

Polymer	CST(sec) at varying polymer dosages(ppm)				
	200	250	300	400	500
Example 2	30	25	18	10	5
Polymer B	20	15	10	5	5
Example 3	30	15	10	5	5
Polymer A	35	12	10	5	5
Example 4	35	10	5	5	12
Polymer D	38	25	15	5	5
Example 5	45	25	15	7	20
Polymer C	100	75	15	8	10

Test 3:

A sample of mixed primary and secondary sludge from a
paper mill was used as the test substrate. The block copolymer
performance was compared to a commercial copolymer containing
5   similar mole % of the cationic monomer used for this type of
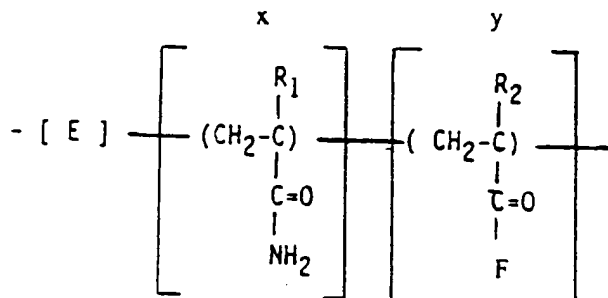application.

Dewatering performance is presented in Table VI.

TABLE VI
Dewatering Performance

10   Polymer   CST(sec) at varying polymer dosages(ppm)

Polymer	25	50	100	150	200
Polymer A	35	18	9	15	30
Example 7	33	12	7	7	7

The above data show that the block copolymers in this invention
15   are effective for sludge dewatering. They also offer the unex-
pected advantage of being more tolerant to overdosing, in that over
the range presented, the CST values do not increase with increasing
polymer dosage, as is the case with commercial polymers.

CLAIMS

1. A water soluble block copolymer comprising the formula:

$$- [E] \left[-(CH_2\text{-}\underset{\underset{NH_2}{\overset{\overset{R_1}{|}}{C=O}}}{C}) - \right]_x \left[(CH_2\text{-}\underset{\underset{F}{\overset{\overset{R_2}{|}}{C=O}}}{C}) - \right]_y$$

wherein E is a polymer obtained from the polymerization of ethylenically unsaturated hydrophobic monomers initiated by a difunctional initiator; x is a nonionic monomer; y is a cationic monomer; R_1 and R_2 are H or a C_1 to C_3 alkyl group; F is a salt of an ammonium cation selected from the group consisting of $NHR_3 N^+ (R_{4,5,6})M^-$ and $OR_3 N^+ (R_{4,5,6})M^-$; wherein R_3 is a C_1 to C_4 linear or branched alkylene group; R_4, R_5 and R_6 are H, C_1 to C_4 linear or branched alkyl, C_5 to C_8 cycloalkyl, aromatic or alkylaromatic; M^- is an anion selected from the group consisting of chloride, bromide, methyl sulfate and hydrogen sulfate; and the molar percentage of x:y is from about 0:100 to 95:5, with the proviso that the total of x+y equals 100%.

2. The block copolymer of claim 1 wherein the ethylenically unsaturated hydrophobic monomer is selected from the group consisting of alkyl acrylate having from 4 to about 16 carbon atoms, higher alkyl esters of ethylenically unsaturated carboxylic acids, alkaryl esters of ethylenically unsaturated carboxylic acids, N-alkyl ethylenically unsaturated amides, vinyl alkylates wherein the alkyl moiety has at least 8 carbon atoms, N-vinyl amides and aralkylstyrenes.
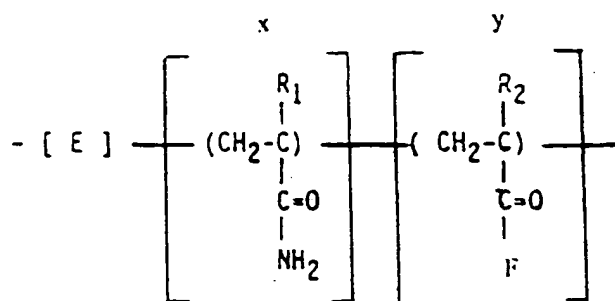
3. The block copolymer of claim 2 wherein the alkyl acrylate is 2-ethylhexyl acrylate.

4. The water soluble block copolymer of claim 1 wherein R_1 is H.

5. The water soluble block copolymer of claim 4 wherein R_2 is H or methyl and F is selected from the group consisting of oxyethyltrimethyl ammonium chloride and amidopropyl trimethyl ammonium chloride.

6.　　The water soluble block copolymer of claim 1 wherein the number average molecular weight of E is about 500 to 1,000,000.

7.　　The water soluble block copolymer of claim 6 wherein the number average molecular weight of E is about 1,000 to 500,000.

8.　　The water soluble block copolymer of claim 7 wherein the number average molecular weight of E is about 5,000 to 200,000.

9.　　A method of treating wastewater comprising adding to said wastewater an effective amount of a block copolymer having the formula:

$$- [\ E\ ] \left[\begin{array}{c} x \\ (CH_2-\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle NH_2}{|}}{\underset{\underset{\displaystyle C=O}{|}}{C}}}) \end{array} \right] \left[\begin{array}{c} y \\ (CH_2-\overset{\overset{\displaystyle R_2}{|}}{\underset{\underset{\displaystyle F}{|}}{\underset{\underset{\displaystyle C=O}{|}}{C}}}) \end{array} \right]$$
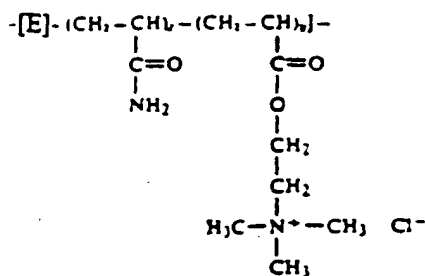
wherein E is a polymer obtained from the polymerization of ethylenically unsaturated hydrophobic monomers initiated by a difunctional initiator; x is a nonionic monomer; y is a cationic monomer; R_1 and R_2 are H or a C_1 to C_3 alkyl group; F is a salt of an ammonium cation selected from the group consisting of $NHR_3\ N^*\ (R_{4,5,6})M^-$ and $OR_3\ N^*\ (R_{4,5,6})M^-$; wherein R_3 is a C_1 to C_4 linear or branched alkylene group; R_4, R_5 and R_6 are H, C_1 to C_4 linear or branched alkyl, C_5 to C_8 cycloalkyl, aromatic or alkylaromatic; M^- is an anion selected from the group consisting of chloride, bromide, methyl sulfate and hydrogen sulfate; and the molar percentage of x:y is from about 0:100 to 95:5, with the proviso that the total of x+y equals 100%.

10.　　The method of claim 9 wherein the ethylenically unsaturated hydrophobic monomer is selected from the group consisting of alkyl acrylate having from 4 to about 16 carbon atoms, higher alkyl esters of ethylenically unsaturated carboxylic acids, alkaryl esters of ethylenically unsaturated

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carboxylic acids, N-alkyl ethylenically unsaturated amides, vinyl alkylates wherein the alkyl moiety has at least 8 carbon atoms, N-vinyl amides and aralkylstyrenes.

11.   The method of claim 10 wherein the ethylenically unsaturated carboxylic acids of the higher alkyl esters are selected from the group consisting of acrylic acid and methacrylic acid.

12.   The method of claim 10 wherein the alkyl acrylate is 2-ethylhexyl acrylate.

13.   The method of claim 9 wherein the nonionic monomer is selected from the group consisting of acrylamide and alkylacrylamide.

14.   The method of claim 13 wherein the nonionic monomer is acrylamide.

15.   The method of claim 9 wherein the cationic monomer is selected from the group consisting of: 2-acryloxyethyltrimethyl ammonium chloride, 3-methacrylamidopropyltrimethyl ammonium chloride, 2-methacryloxyethyltrimethyl ammonium chloride and diallyl dimethyl ammonium chloride.

16.   The method of claim 9 wherein said block copolymer has the formula:

$$-[E]-(CH_2-CH)_x-(CH_2-CH)_y-$$
$$\begin{array}{cc} | & | \\ C=O & C=O \\ | & | \\ NH_2 & O \\ & | \\ & CH_2 \\ & | \\ & CH_2 \\ & | \\ H_3C-N^+-CH_3 \quad Cl^- \\ & | \\ & CH_3 \end{array}$$
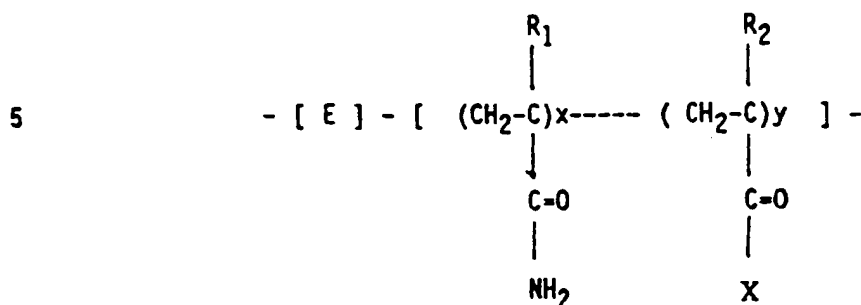
wherein E is a polymer of 2-ethylhexyl acrylate.

17.   The method of claim 9 further comprising dewatering sludge.

18.   The method of claim 9 further comprising clarifying water.

ABSTRACT OF THE DISCLOSURE

A composition and method of use thereof for the treatment of wastewater comprising a block copolymer having the formula:

$$- [\ E\ ] - [\ (CH_2\text{-}C)x ----- (\ CH_2\text{-}C)y\ ] -$$

with R_1 and $C=O$, NH_2 substituents on the x unit and R_2 and $C=O$, X substituents on the y unit.

wherein E is a polymeric segment obtained from the polymerization of hydrophobic monomers, x when present is a nonionic monomer, y is a cationic monomer, R_1 and R_2 are the same or different and are H or a lower alkyl group from C_1 to C_3 and X is a salt of an ammonium cation.

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